

In situ IR study of Catalytic Decomposition of NO on Pd-based catalysts

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Introduction

NO is one of the major pollutants in the exhaust of various combustion processes. The growing concerns for the environment have prompted increasingly stringent NO emission standards. Removal of NO from the automobiles, power plant exhaust streams and other combustion processes has consequently become a challenging task.

Depending on the nature of combustion processes, various catalytic and non-catalytic schemes have been devised to remove NO from exhaust streams. Catalytic approaches for the removal of NO include (i) the reaction of NO with CO over Rh-Pt and Pd-based catalysts in the catalytic converter, (ii) the reaction of NO and CO on metal oxides(1-3), (iii) the selective catalytic reduction (SCR) of NO with NH_3 (4) and (iv) the direct decomposition of NO over Cu-based catalysts (5). Rh-Pt and Pd catalysts (three-way catalysts) have been successfully commercialized to simultaneously remove NO, CO, and hydrocarbons from automobile exhausts. Due to the high cost of noble metals (Rh and Pt), extensive research has been aimed at development of Pd based catalysts for removal of NO from exhaust streams. Although three-way catalysts work well for controlling the emission of pollutants from the current mode of operation for the internal combustion engine, the effectiveness of the three-way catalyst decreases dramatically as the composition of flue gas deviates from those produced by the stoichiometric combustion of gasoline. The selective catalytic reduction of NO with NH_3 suffers from the disadvantage that catalytic reduction with ammonia requires the special handling and storage of ammonia and a special metering system to avoid NH_3 slippage.

The direct decomposition of nitric oxide to benign nitrogen and oxygen is thus the most attractive approach for the control of NO emissions because of its simplicity (6). The direct decomposition of $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$ is thermodynamically favorable at temperatures below 2000 K. Development of an active NO decomposition catalyst will eliminate the use of reducing agents as hydrocarbons, NH_3 and CO thereby reducing the cost of NO removal. Cu-ZSM-5 has been reported to have the highest activity for NO decomposition catalysts among the catalysts tested. The rapid deactivation effect of H_2O and its susceptibility to SO_2 poisoning has severely limited its practical application.

Objective

The objective of this paper is to investigate the activity of Pd based catalysts for NO decomposition. Successful development of Pd-based catalysts for the catalytic decomposition of NO has been attributed to its excellent durability and its relatively low cost compared to Rh/Pt. Studies on the proposed elementary steps for NO decomposition reaction have revealed that the inability of the catalyst to desorb the oxygen produced from NO dissociation to be the reason for its low activity (7). An approach to remove the oxygen from these catalysts is the use of rare earth oxides such as ceria and terbium oxide as promoters. A novel approach is to use carbon as a support for the catalyst system thus enabling the removal of oxygen by the formation of CO_2 . Pd/ Al_2O_3 and Pd/C have thus been investigated for NO decomposition activity. *In situ* infrared spectroscopy (IR) coupled with mass spectrometry (MS) were employed to determine the nature of active adsorbate for NO decomposition and the concentration of gaseous products.

Experimental

The catalysts used for this study, 2wt% Pd/ Al_2O_3 and 2wt% Pd/C were prepared by incipient wetness impregnation technique with PdCl_2 solution at a pH of 2.8 and 60 °C. The catalysts were calcined in air at 673 K for 8 h and then reduced at 673 K in flowing H_2 for 8 h (8).

FTIR was used to monitor the adsorbate concentrations and mass spectrometry to analyze the change in the concentration of the gaseous product from the effluent of the IR

reactor cell described in detail elsewhere (9). DRIFTS was employed to study the adsorbate concentrations on carbon supported catalyst because of the inability to use Transmission IR on carbon based catalysts as carbon has the capability to adsorb the IR beam.

Results

NO Decomposition on Pd/Al₂O₃

Figures 1 and 2 show the MS response of effluent of IR reactor cell and the IR spectra of adsorbates during the step switch from He to NO at 473 K. Exposure of the catalyst to the NO step flow causes an initial overshoot in the N₂ MS response indicating that the catalyst has high activity at the beginning. Absence of NO in the effluent stream indicates a near 100% conversion. A band at 1802 cm⁻¹ due to Pd-NO⁺ appears after 2.9 min reflects the increase in the concentration of Pd⁺ by adsorbed oxygen from NO dissociation. Prolonged exposure of the catalyst to NO causes an increase in the intensity (i.e., surface coverage) and wavenumber of Pd-NO⁺.

After 20 min, (i) decrease in the N₂ formation, (ii) increase in the N₂O formation, (iii) increase in O₂ MS response and (iv) breakthrough in the NO MS response have been observed. These changes are an indication of a drop in the catalyst activity by accumulation of adsorbed oxygen on the surface which blocks the sites required for NO dissociation. The evolution of oxygen indicates that the catalyst exhibits an ability to desorb oxygen after the saturation is reached. The tendency of the Pd/Al₂O₃ catalyst to desorb oxygen after reaching the saturation level of oxygen aids in controlling a complete loss in the activity as evidenced by continuous formation of N₂ and N₂O for 55 min after NO breaks through. The increase in the amount of adsorbed oxygen affected the formation of N₂. The formation N₂O could be due to its role as an intermediate for N₂ formation which stops after the catalyst deactivates. High NO coverage favors N₂O formation by the reaction of adsorbed NO with adsorbed N.

NO Decomposition on Pd/C

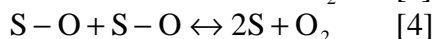
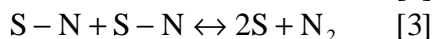
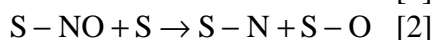
Figures 3 and 4 show the MS response of effluent of IR reactor cell and the IR spectra of adsorbates during the step switch from He to NO at 473 K. Response of N₂ is

similar to that observed on Pd/Al₂O₃. The catalyst shows higher period of activity, takes 45 min for the deactivation of the catalyst, compared to that of Pd/Al₂O₃.

Pd-NO at 1770 cm⁻¹ appears after 20 min and continues to increase in intensity after concentration of NO breaks through. The lack of sharpness in the quality of IR spectra is due to high capability of carbon for adsorbing the IR beam. The N₂O formation starts before the breakthrough in the NO MS response. Following the breakthrough of NO, the MS responses of N₂, and O₂ are comparable to those observed on Pd/Al₂O₃. Comparison of the marginal activity period leads us to conclude that the carbon supported catalyst has promoted NO dissociation.

Discussion

The role of oxygen desorption in NO decomposition has been previously discussed and our recent studies (7) have suggested that the NO decomposition may occur via the following steps:



The continue increase in the Pd-NO⁺ intensity prior and after a drop in catalyst activity (an increase in the concentration of gaseous NO) leads to conclude that Pd-NO⁺ is a spectator for the NO dissociation (step 2). The absence of another IR-observable species prevented us from verifying the nature of NO adsorbate in step 2. Step 2 and 3 are facile steps at 673 K as evidenced by high conversion.

If the breakthrough in NO concentration is used as an index for measuring the activity, we can conclude that Pd/C is more active than Pd/Al₂O₃ since it exhibited higher period of activity (50 min compared to 20 min). The difference in activity could be due to the availability of the number of the Pd sites for NO dissociation. Carbon may provide higher surface area compared to Al₂O₃ which can delay the breakthrough in the NO concentration by accommodation of large fraction of adsorbed oxygen.

The formation of N₂ (step 3) depended on the surface coverage of adsorbed N from NO dissociation. The absence of steric crowding of adsorbed NO on the surface led

to an overshoot in the formation of N_2 at the beginning of the step switch of NO on the catalyst. The lack of oxygen formation (step 4) during 100% NO conversion suggests that the NO conversion to N_2 is not a catalytic process instead it is stoichiometric. A process is defined catalytic when active sites are regenerated and the products formation is continuous. The inability of both catalysts to desorb oxygen during the high NO conversion is further evidenced by the absence of NO_2 formation by the reaction of adsorbed NO with adsorbed O (10).

Future Studies

Efforts are being made to search for NO decomposition catalysts which can expel the adsorbed oxygen from the surface and regenerate the sites for NO decomposition, thereby increasing the activity of the catalyst. Attempts are being made to use promoters like Pr for NO decomposition catalyst which would enable the desorption of oxygen from the surface.

References

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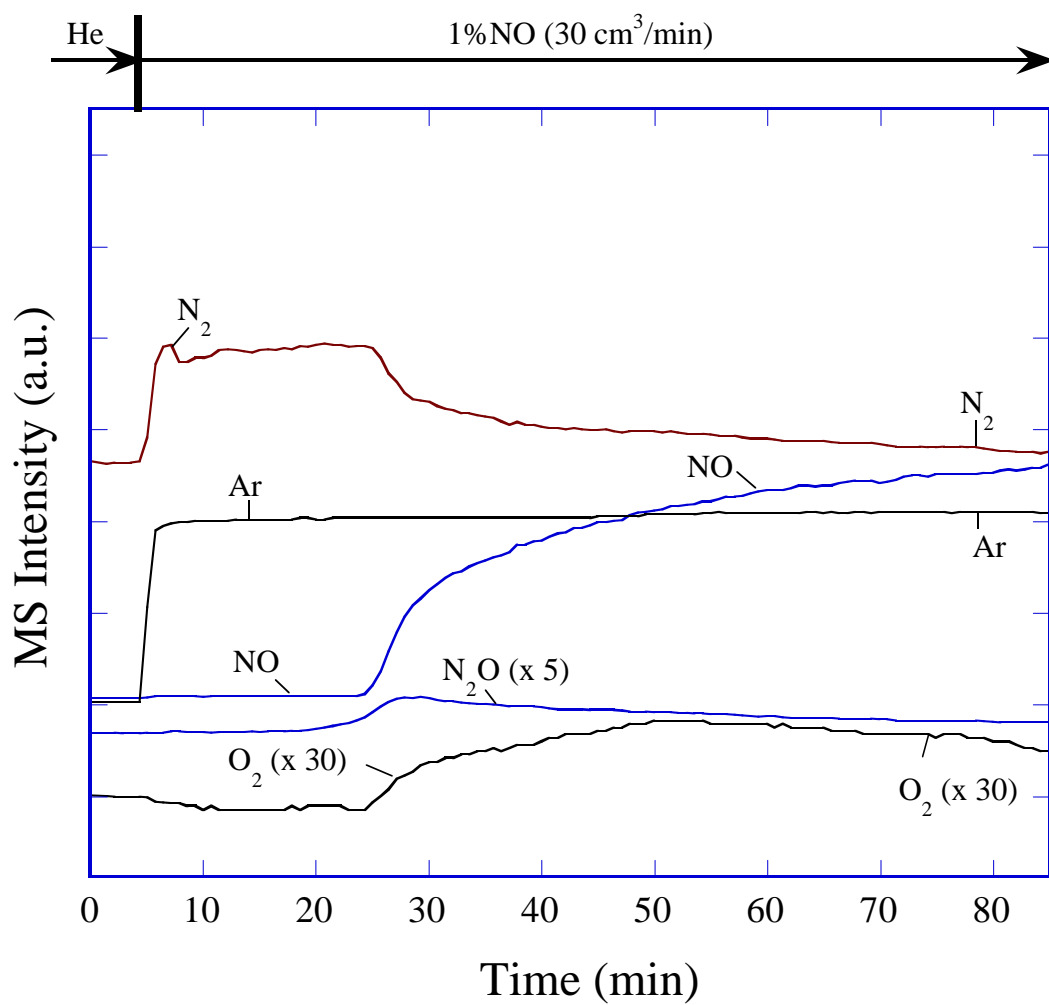


Figure 1 MS analysis of Effluent of IR Reactor Cell during the Step Switch from He ($30 \text{ cm}^3/\text{min}$) to 1%NO ($30 \text{ cm}^3/\text{min}$) on $\text{Pd}/\text{Al}_2\text{O}_3$ at 673 K.

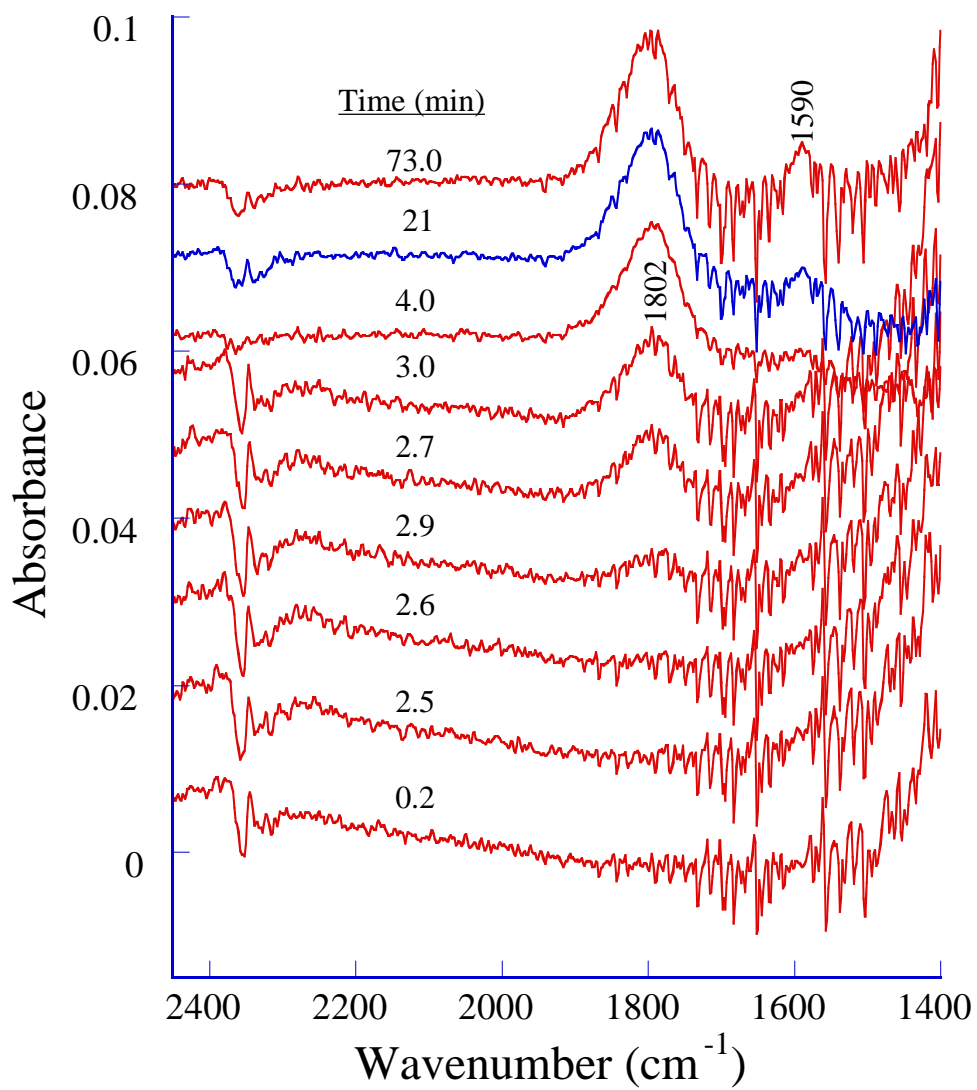


Figure 2 IR Spectra of Adsorbates during the Step Switch from He (30 cm³/min) to 1%NO (30 cm³/min) on Pd/Al₂O₃ at 673 K.

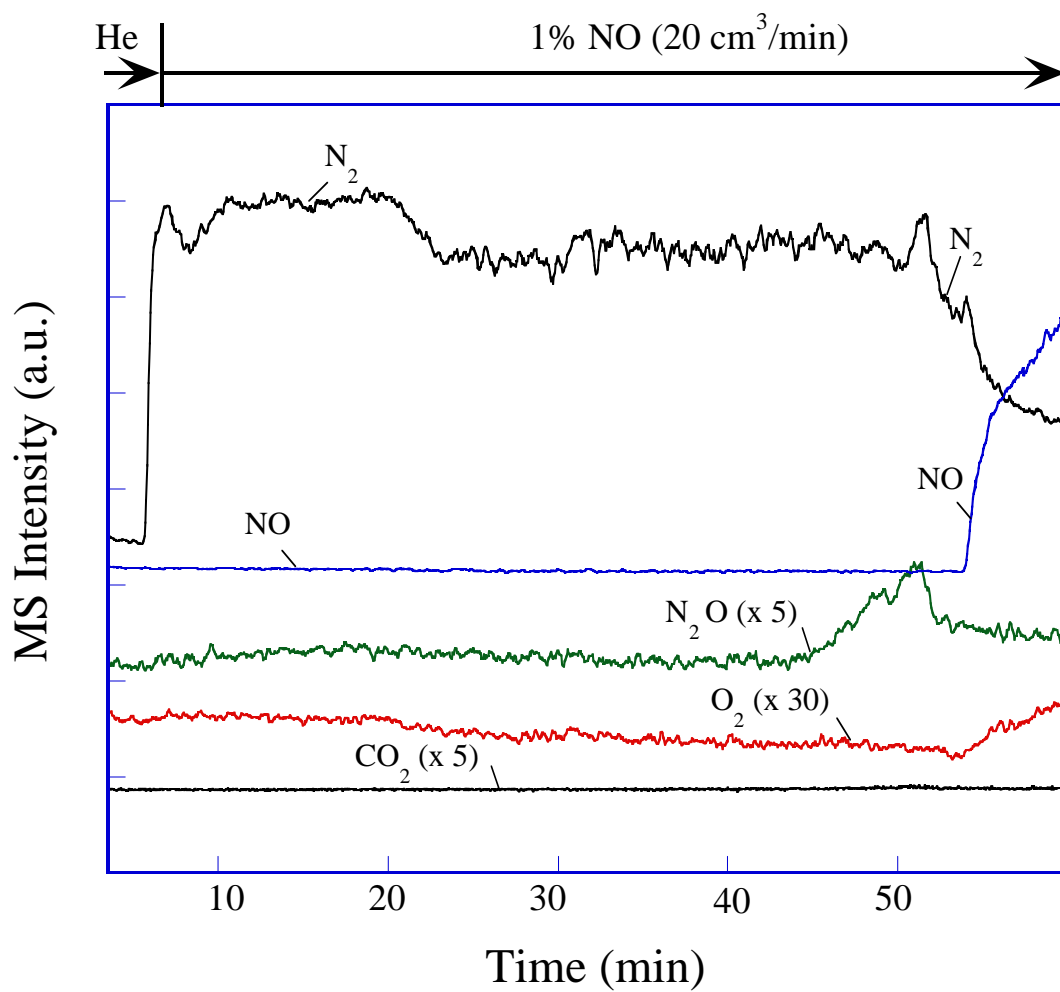


Figure 3 MS analysis of Effluent of IR Reactor Cell during the Step Switch from He (20 cm³/min) to 1%NO (20 cm³/min) on Pd/C at 673 K.

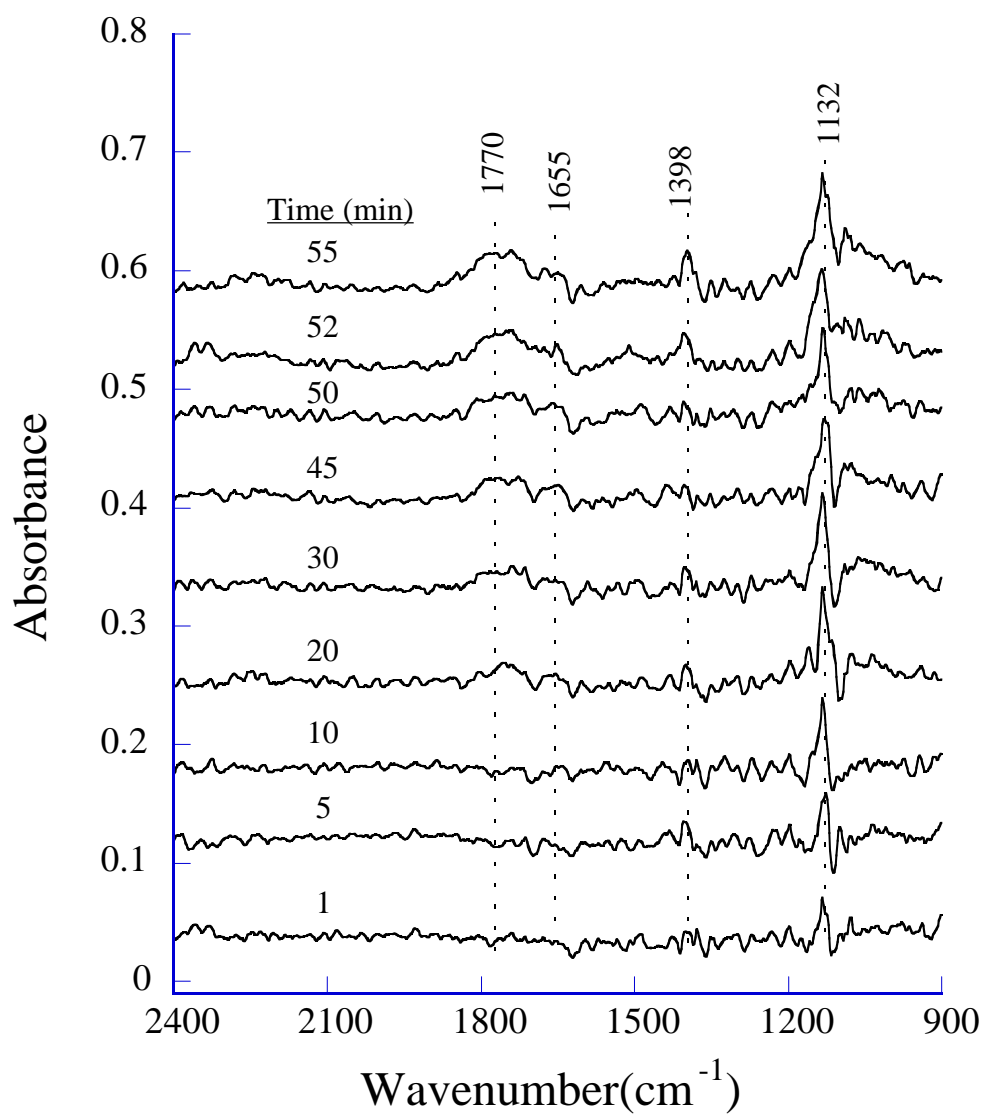


Figure 4 IR Spectra of Adsorbates during the Step Switch from He ($20 \text{ cm}^3/\text{min}$) to 1%NO ($20 \text{ cm}^3/\text{min}$) on Pd/C at 673 K.